STRUCTURE OF THE SPECTRUM OF SINGLY IONISED BROMINE

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Plates XII & XIII

ABSTRACT. The earlier analysis is revised in several respects and very much extended. 76 levels belonging to the $4p^4$, $4p^5$, 5s, 4d, 5p, 6s, 5d and 4f configurations are newly identified involving the classification of nearly 400 additional lines in the region 10000 A in the photographic infra-red, to 350 A in the vacuum ultraviolet. This brings the total of classified lines to about 540. Almost all the intense lines are classified except about a dozen and some faint lines. The second ionisation potential is established to be 21.80 volts.

INTRODUCTION

Besides the very early work summarised in Kayser's Handbuch der Spectroscopie, Vol. 8, the previous important work on the description and analysis of the spectrum of singly ionised bromine consists essentially of the investigations of Bloch and Bloch (1927), Bloch, Bloch and Lacroute (1934), Lacroute (1935), Tolansky and Trivedi (1940), Ramanadham and Rao (1944), and Ranade (1951). Bloch and Bloch (1927) have first given a fairly extensive and accurate wavelengths of the lines of bromine between 6750 and 2250A using a source of electrodeless discharge and later, along with Lacroute (1934), reported the identification of 45 levels of Br II based on the ^4S and ^2D states of the Br III ion, involving the classification of about 170 lines, and have also given from Zeeman effect studies, the values of the g-factor for some of the levels Lacroute (1935) has measured the spectrum in the region 2280–649 A as recorded on a 1-metre vacuum grating spectrograph using a source of electrodeless discharge similar to the one employed by Bloch and Bloch (1927) and confirmed some of the levels by a study of the Zeeman effects. The Zeeman patterns of several other lines also were recorded.

Ramanadham and Rao (1944) have revised and extended the earlier analysis. They have made changes in the designations and values of the 4d $^3D^0$ and $^1D^0$ levels to bring them into conformity with their positions in isoelectronic and analogous spectra and assigned the $^5D^0$ term identified earlier to the 5d instead of the 4d configuration as the latter is expected to be deeper than the 4d $^3D^0$

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term and of the same order of magnitude as the $5s$ terms. They have rejected the levels given in the earlier investigation as $5s'\ {}^1D_2{}^0$ and $5d'\ {}^3D_2{}^0$ as unreal since combinations with them occur elsewhere and omitted the levels given by the previous workers as $4d\ {}^3D_{2,1}{}^0$ since their reality could not be well established though some combinations with the 5p terms and with $4p^4\ {}^3P_2$ were present. They have further identified the $4p^4\ {}^3P_{0,1}$, $5p'\ {}^3F_4$ levels, $5d\ {}^3D^0$ term and several $5d'$ levels. The $6s'$ levels are also given by them but as tentative.

Tolansky and Trivedi (1940) reported measurements of the hyperfine structure for four lines of Br II. Ranade (1951) has analysed the hyperfine structure of some lines and confirmed the analysis of the combinations involving the deeper terms given by Bloch, Bloch and Lacroute (1934).

Moore (1952) has compiled all the energy levels in the book "Atomic Energy Levels, Vol. II" in the ascending order of magnitude with the ground level $4p^4\ {}^3P_2$ as zero and has calculated the g-values for some of them with the help of the Zeeman patterns obtained by Lacroute. She has also suggested that the levels 96439.4 and 98807.3 given by Bloch, Bloch and Lacroute as $4d\ {}^3D_{2,1}{}^0$ and omitted by Ramanadham and Rao might be $4p^5\ {}^3P_{2,1}{}^0$ levels.

Still several and some very strong lines in the spectrum remain unclassified and as remarked by Moore in the book referred to above the analysis is far from complete and well worth further observation. Some of the levels identified in previous work need confirmation and on close scrutiny other levels appear to be either unreal or not correct in designation. In the present work an extensive study of the spectrum over the entire range from the photographic infra red to the vacuum ultraviolet (10000 to 350A) is made with the purpose of obtaining a complete analysis of the spectrum. As a result, several new levels belonging to the $4p^4$, $4p^5$, $4d$, $5s$, $5p$, $5d$, $6s$ and $4f$ configurations are identified leading to the classification of nearly 400 additional lines bringing the total of classified lines to about 540. Almost all the intense lines are now interpreted except for about a dozen and some faint lines.

A preliminary note giving the newly identified levels is already published (Bhupala Rao, 1956).

EXPERIMENTAL

The source of radiation chiefly used in this investigation is a H-shaped pyrex glass discharge tube with a capillary of 1 to 2 mm. in diameter and about 2 cm. in length excited by a transformer giving 20000 V in the secondary. In the uncondensed discharge tube, the arc lines of bromine and a few lines involving combinations between deep levels of Br II appear. When the pressure is low the capillary is light red in colour and this is the condition best suited for obtaining the arc lines. As the gas pressure is increased the colour of the discharge in the capillary changes to greyish blue and some of the prominent first spark lines also appear. Kiess and de Bruin (1929) have reported a similar observation. Most of the arc lines occur in the infra-red while the resonance group $4s^2$ $4p^5$ $^2P^0$-$4s^2$—$4p^4$ $(^3P)5s$ ^4P, ^2P is in the region 1650 to 1300 A. In the condensed discharge with a condenser of capacity approximately 1.8×10^{-3} mfd kept in parallel with the transformer, the colour of the discharge in the capillary is bluish white and all the lines due to the singly and doubly ionised atoms are recorded with good intensity while the arc lines are generally diminished in intensity though some of them in the infra-red appear fairly strong. As one goes to lower wavelengths, lines due to still higher stages of ionisation also appear with comparable intensity. When an inductance of 0.5 m.h. is introduced into the circuit in series with the discharge tube, the intensity of Br II lines remains unchanged or even increases in several cases. But the lines of Br III are either partially or completely suppressed except in the vacuum ultraviolet region where they also appear fairly intense.

The discharge is also excited by 10000 V rectified by a kenotron 8013A and condensed by capacities of (a) 0.5 m.fd. and (b) 0.2 m.fd. In this condition, particularly with 0.5 m.fd and narrow capillary, a strong background is generally present and all the important lines of the various stages of ionisation appear. When an inductance of 0.5 m.h. is introduced in series with the discharge tube, the intensity of the background is reduced

The spectrum is obtained also in a high frequency discharge tube using a 100-watt H.F. oscillator operating at a frequency of about 11 M.c/s. In the visible region several lines of Br I, a few lines of Br II and a good number of bands of bromine molecule appear. But in the near ultraviolet only a fairly strong continuum is recorded. Again below 2000 A the bands of bromine molecule appear.

The spectrum is phographed in the infra-red on Kodak I.Q. and I.N. plates with Fuess and Hilger Glass Littrow spectrographs. In the vacuum ultraviolet region 1-metre Normal Incidence Vacuum Grating spectrograph set up by the author in this laboratory is used, (15000 lines per inch); the grating was kindly supplied by Prof. Siegbahn. The spectrum is recorded on Ilford Q_2 plates and extends upto 350 A with 6 hours exposure in condensed discharge condition.

In addition to the data obtained from the above methods a large number of photographs were also kindly made available to the author by Prof. K. R. Rao. These are pictures taken at Upsala with a Grazing Incidence Spectrograph long ago and well preserved, extending from 1085 to 480 A. The dispersion about 3.2 A/m.m. near 950 A. The source consisted of a vacuum spark between electrodes tipped with Rb Br and Cs Br ; full details regarding the pictures are given by Rao and Badami (1931) in the paper on Se IV.

The important multiplets involving the newly identified levels are given in Tables II to VI. The intensities for the lines specified there are the intensities in condensed discharge with inductance. Newly classified lines not contained in the multiplet tables are given separately in Table VIII with their intensities in condensed discharge with inductance, wavelengths and wavenumbers. All the values above 2000 A are from Littrow measurements.

ANALYSIS

The predicted terms of Br II are given in Table I. The observed terms are all underlined and those identified in previous investigations are marked with an asterisk also. All the newly observed energy levels are given in the preli-

TABLE I

Terms of Br II

Configuration	Terms		
$4s^2\ 4p^4$		$\underline{^3P^*}$ $\underline{^1D}$ $\underline{^1S}$	
$4s\ 4p^5$		$\underline{^3P^o}$ $\underline{^1P^o}$	
Basic terms of Br III	^4S	^2D	^2P
$4s^2\ 4p^3$			
$4s^2\ 4p^3\ 5s$	$\underline{^5S^o*}$	$\underline{^3D^o*}$	$\underline{^3P^o*}$
	$\underline{^3S^o*}$	$\underline{^1D^o*}$	$\underline{^1P^o}$
$4s^2\ 4p^3\ 5p$	$\underline{^5P^*}$	$\underline{^3F^*}$ $\underline{^3D^*}$ $\underline{^3P^*}$	$\underline{^3D}$ $\underline{^3P}$ $\underline{^3S}$
	$\underline{^3P^*}$	$\underline{^1F^*}$ $\underline{^1D^*}$ $\underline{^1P^*}$	$\underline{^1D}$ $\underline{^1P}$ $\underline{^1S}$
$4s^2\ 4p^3\ 4d$	$\underline{^5D^o}$	$^3G^o$ $\underline{^3F^o}$ $\underline{^3D^o}$ $^3P^o$ $^3S^o$	$^3F^o$ $^3D^o$ $^3P^o$
	$\underline{^3D^o*}$	$\underline{^1G^o}$ $\underline{^1F^o}$ $\underline{^1D^o}$ $^1P^o$ $^1S^o$	$^1F^o$ $^1D^o$ $^1P^o$
$4s^2\ 4p^3\ 6s$	$\underline{^5S^o*}$	$\underline{^3D^o}$	$\underline{^3P^o}$
	$\underline{^3S^o*}$	$\underline{^1D^o}$	$\underline{^1P^o}$
$4s^2\ 4p^3\ 5d$	$\underline{^5D^o*}$	$\underline{^3G^o}$ $\underline{^3F^o*}$ $\underline{^3D^o}$ $\underline{^3P^o}$ $\underline{^3S^o}$	$^3F^o$ $^3D^o$ $^3P^o$
	$\underline{^3D^o*}$	$\underline{^1G^o}$ $\underline{^1F^o}$ $\underline{^1D^o}$ $\underline{^1P^o}$ $^1S^o$	$^1F^o$ $\underline{^1D^o}$ $\underline{^1P^o}$
$4s^2\ 4p^3\ 4f$	$\underline{^5F}$	^3H $\underline{^3G}$ $\underline{^3F}$ $\underline{^3D}$ $\underline{^3P}$	^3G ^3F ^3D
	$\underline{^3F}$	$\underline{^1H}$ $\underline{^1G}$ $\underline{^1F}$ $\underline{^1D}$ ^1P	^1G ^1F ^1D

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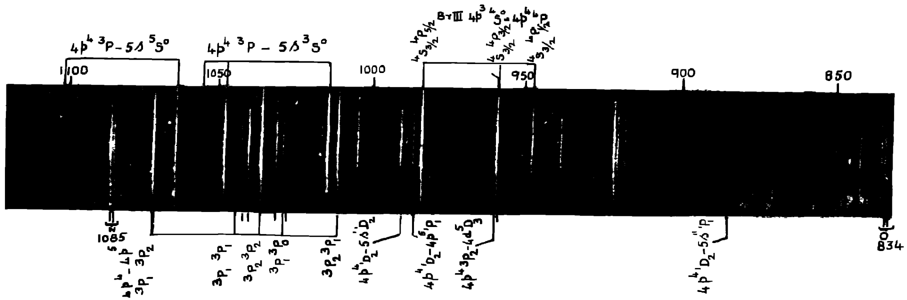
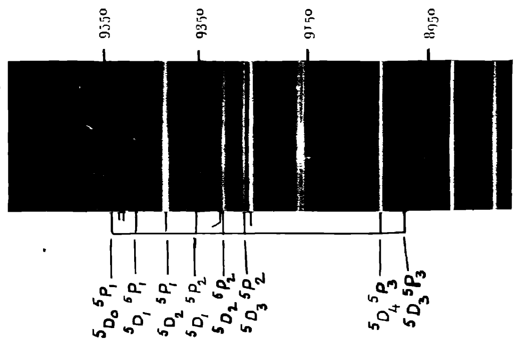
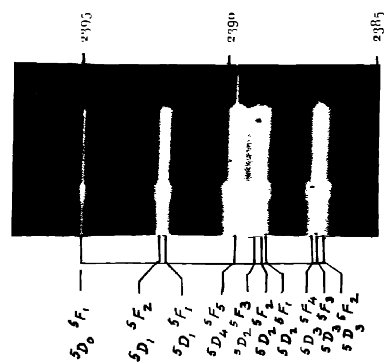


a 4p⁴ ³P − 4p⁵ ³P⁰, 4p⁴ ¹P − 5s³ S⁰ and 4p⁴ ³P − 5s³ S⁰ multiplets



4 d⁵ D⁰ − 5 p⁵ P multiplet



4 d⁵ D⁰ − 4 f⁵ F multiplet

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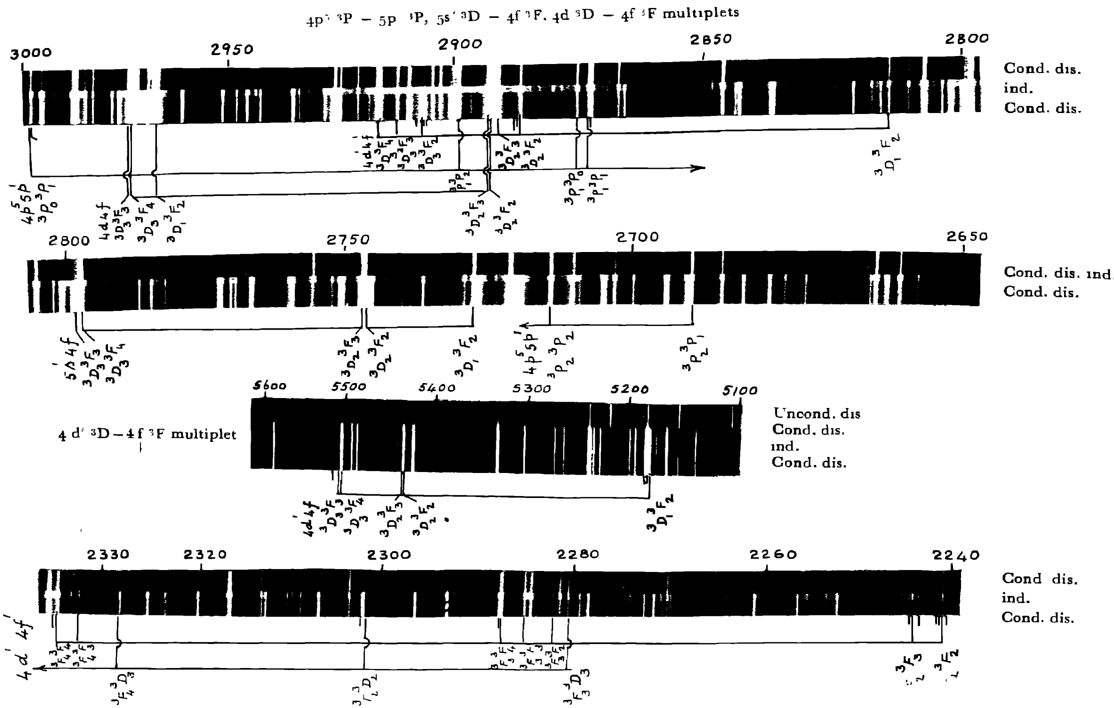
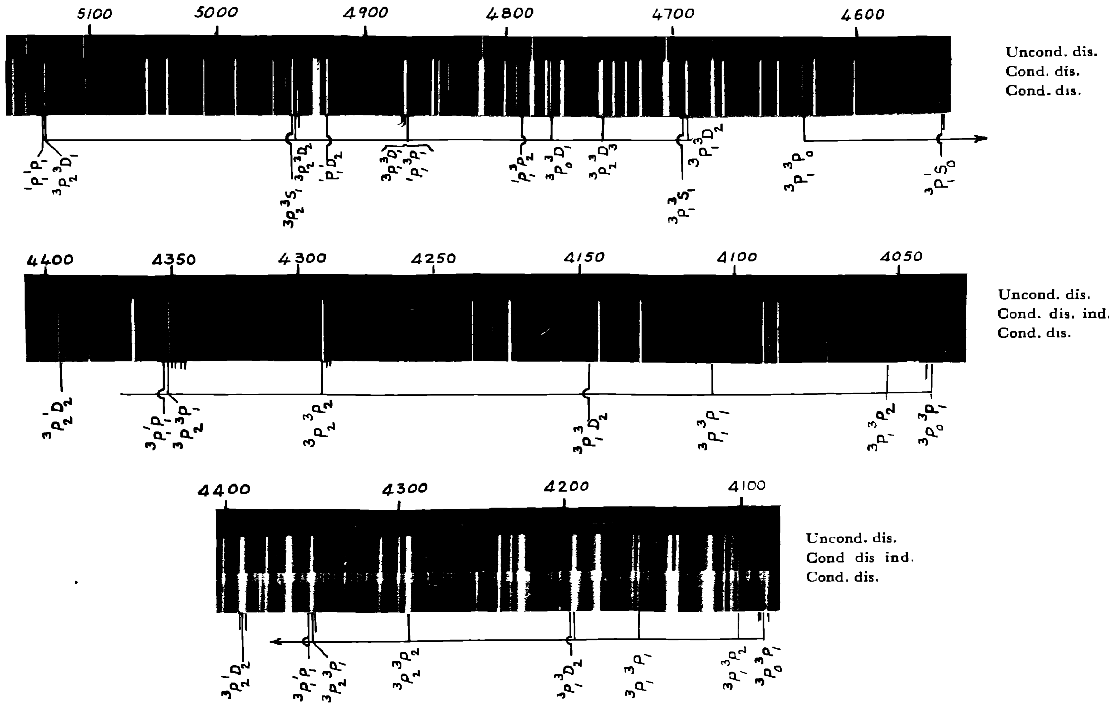
PLATE XII B





5 s'' − 5 p'' multiplets.

minary note (Bhupala Rao, 1956). Several of them are contained in the multiplet tables also. The rest are given in Table VII. The values of some of the levels of 4d $^5D^0$, 4f ^5F and ^3F terms differ slightly from those given in the preliminary note since these had to be readjusted in the final calculation. The levels 161526.4 and 161896.2 appearing as 4f$''^1D_4$ and 4f$''^1G_2$ in the preliminary note are actually 4f$'$ $^1G_4$ and 4f$'$ $^1D_2$ respectively.

The lines 98476, 95336 and 93921 cm^{-1} (1015.5, 1048.9 and 1064.7 A respectively) in the vacuum ultraviolet region are very prominent and longer than the other lines [Plate XII A (i)] which suggest that they form the resonance lines. Their intensity and characteristics confirm the identification of the 4p^4 ^3P levels. The lines, 98804, 96430 and 93295 cm^{-1} (1012.1, 1037.0 and 1071.9 A respectively) also shown in Plate XII A(i) are equally strong and have the same characteristics as the resonance lines lending strong support to the suggestion that the levels 96439.4 and 98807.3 may be 4p^5 $^3P^0{}_{2,1}$ levels. Hence it is accepted as the correct designation of the two levels and only the 4p^5 $^3P^0{}_0$ level remains to be identified. These two levels give combinations with several 4p^4, 5p, and 5p$'$ levels. The multiplet 4p^5 $^3P^0$ 5p$'$ ^3P is particularly well developed giving intense lines (Plate XII B). A comparison of the values and intervals of the $4p^5$ $^3p^0$ levels with those in Kr III (Humphreys, 1935 and Boyce, 1935) leads to a value of about 1400 cm^{-1} for the 4p^5 $^3P_0{}^0$—$^3P_1$ interval, by which the 4p^5 $^3P_0{}^0$—5p$'$ $^3P_1$ line should be in the region of ν 33400 cm^{-1}. From an examination of the plate for a line in that region with the same characteristics as the other lines of the multiplet, the line 33358.9 cm^{-1} is identified to be the 4p^5 $^3P_0{}^0$—5p$'$ $^3P_1$ combination. It is confirmed by the combinations of the resulting level 100242.2 with seven other even levels.

The 4p^5 $^1P_1{}^0$ level is expected to give strong lines with 5p$'$ $^1D_2$ and 5p$'$ $^1P_1$ levels. Ramanadham and Rao have suggested the 5d$'$ $^1P_1{}^0$ level entirely by the pair of lines 17481.6 and 23364.4 cm^{-1}. But this pair is found to be more completely suitable for the 4p^5 $^1P_1{}^0$ level of magnitude 113342.8 cm^{-1} which is consistent with the expected value from a study of the analogous spectra. Its combinations with twelve other even levels confirm the identifications. The combinations of the 4p^5 levels with the even levels are given in Tables II to IV.

Of the remaining unclassified lines, the group of close lines at 41800 cm^{-1} (2390 A) stands most prominent appearing prominently even under the weakest excitation including the uncondensed discharge. An attempt was made at first to see if they could be accounted for as combinations involving 5p and 5p$'$ terms, but this attempt proved unsuccessful. A close examination of the lines shows they are all very diffuse and have strong satellites very close to them. A study of the position of the 4d $^5D^0$ term in the isoelectronic sequence Se I, (Ruedy and Gibbs, 1934) Br II, Kr III leads to a value of about 104000 cm^{-1} in Br II.

TABLE II

Odd levels	Even levels	$4p^4$ $^3P_0$ 3840	$^3P_1$ 3139	$^3P_2$ 0	$5p$ $^5P_1$ 114682 8	$^5P_2$ 114818 1	$^5P_3$ 115176.2	$^3P_0$ 117834.3	$^3P_1$ 117561.5	$^3P_2$ 117767.6
$4p^5$ $^3P_0$	100242.2		97098 (1)							
$^3P_1$	98807.3		95658 (2)	98804 (6)		16011 3 (1)		19027.4 (1)	18754.5 (8)	18960.4 (6)
$^3P_2$	96439.4		93295 (6)	96430 (6)	18243 3 (2)		18736.9 (2)		21122.2 (1)	21327.8 (00)
$4d$ $^5D_0$	104206.1		101055 (0)		10477 (1)					
$^5D_1$	104151.7		101002 (0)		10531 (3)	10666 (0)				
$^5D_2$	104086.1				10597 (6)	10732 (2)				13680 (2)
$^5D_3$	104044.6			104042 (0)		10774 (4)	11132 (2)			13722 (1)
$^5D_4$	104097.9						11078 (7)			
$4d'$ $^3F_2$	117744.6									
$^3F_3$	118509.1			118498 (1)						
$^3F_4$	119432.1									
$^3D_1$	126788.2	122945 (1)	123651 (0)	III? 126794 (00)						
$^3D_2$	127687.7		124544 (3)	127688 (0)						
$^3D_3$	127940.6			127939 (2)						10171 (1)
$^1D_2$	128890.5		125751 (00)	128881 (1)			(I) 13713 (00)			

Assuming the 4f orbit to be hydrogen like, the value of 4f ^5F term is most likely to be of the order of 146000 cm^{-1} and the 4d $^5D^0$—4f ^5F multiplet should then be expected in the neighbourhood of 42000 cm^{-1}. From these considerations the group at 41800 cm^{-1} is classified as the 4d $^5D^0$ 4f ^5F multiplet. This classification is confirmed by the presence of the entire multiplet 4d $^5D^0$—5p ^5P in the region 10500-11000 cm^{-1} and supported by several intercombinations. These two multiples are shown in Plates XII A(i) and (ii). Further confirmation is obtained by the identification of the 4f ^3F term within 200 cm^{-1} from the 4f ^5F term giving very strong combinations with 5s′ $^3D^0$, $^1D^0$ and 4d $^3D^0$ and 4d′ $^3D^0$ terms. [Plates XII A(ii), (iii) and XIIB]. These multiplets are given in Tables II and V.

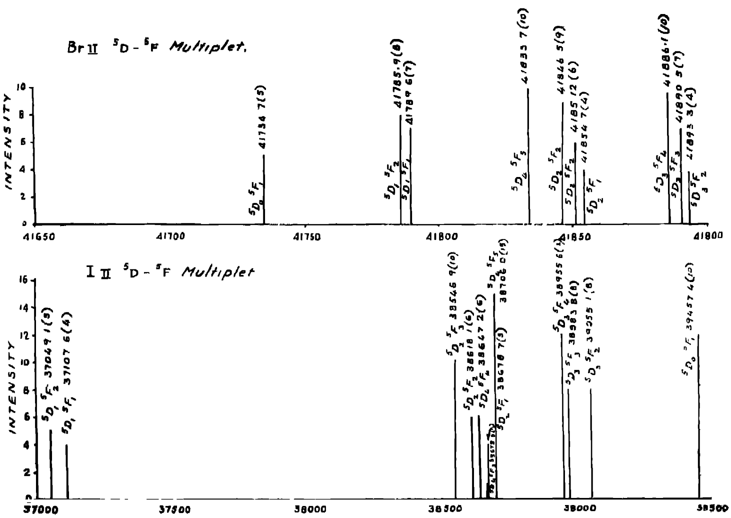


Fig. 1

In the spectrum of singly ionised iodine, Murakawa (1938) has classified a similar group as 5d $^5D^\circ$—5f ^5F multiplet. A plot of this multiplet in Br II and I II presented in figure 1 brings out the similarity between the two. Here it may be observed that this ^5F term of absolute value 28600 cm^{-1} in I II may more probably belong to the 4f electron consistent with its hydrogen like nature. On this basis the absolute value of the 5f term will be of the order of 17600 cm^{-1}. In Cl II also Murakawa (1935) has identified a term as 4f ^3F but Kiess and de Bruin (1939) have rejected the suggestion on the ground that the term does not exhibit the combination characteristics of ^3F terms though its magnitude is of the correct order, its combinations are sharp without shading or satellites. But in view of the identification of the corresponding multiplet in Br II and III it is likely that there may be scope for further consideration of the assignment given by Murakawa.

Ramanadham and Rao have based the identification of the $5s''$ $^3P^o$, $^1P^o$ terms purely on combinations with the ground term in the vacuum ultraviolet region. The $5s''$ $^3P^o$ levels are of the right order of magnitude and are confirmed by the new combinations identified in this investigation. But the $5s''$ $^1P_1{}^0$ level given by them is based on only a single combination 105377 cm^{-1} with the level 11409 (absolute value 162710 in their paper); this level 11409 is found to be unreal, the line 105377 cm^{-1} defining this level having been distinctly classified as Br III $4p^3$ $4S_{3/2}$—$4p^4$ $^4P_{1/2}$ combination (Bhupala Rao, 1956a). Further, the value 116786 (absolute value 57333.0 in their paper) for the $5s''$ $^1P_1{}^0$ level is too deep and not consistent with the progression of values in spectra isoelectronic with BrII.

The 5p″ levels are estimated to be of the order of 144000 cm^{-1}. With the help of the 5s″ $^3P^0$ intervals which are already identified, the 5p″ ^3D levels could be established easily by searching for the appropriate interval and are confirmed by the presence of the 5s′ $^3D^0$—5p″ ^3D and 4d $^3D^0$—5p″ $^3D^o$ multiplets. But the identification of the 5p″ ^3P term has proved to be more difficult because of the intensity anomalies in the 5s″ $^3P^0$—5p″ ^3P multiplet, the great irregularity in the variation of the intervals between its levels and the few combinations it gives with the 5s′ $^3D^0$, 4d $^3D^0$ and $4p^5$ $^3P^0$ term. It may be noted, however, that a similar intensity anomaly in the 5s″ $^3P^0$—5p″ ^3P multiplet and irregularity in the intervals of the 5p″ ^3P term are present in Kr III also. Some of the lines included in this multiplet were classified by Ramanadham and Rao as combinations between 5p′ and 5d′ terms. But the present assignment seems to be more consistent and appropriate. The two levels 144517.7 and 145370.0 are designated as 5p″ $^1P_1$ and 5p″ $^1D_2$ respectively due to their combining properties. With the help of the interval between these, the 5s″ $^1P_1{}^0$ level is found to be 125058.7 which is supported by several intercombinations. The scheme of all these combinations is given in Table IV. The 5s″—5p″ multiplets are shown in Plate XIII.

The $4p^4$ $^1D_2$ level was suggested by Ramanadham and Rao on the basis of two lines 101532 (10) and 98284 (0) cm^{-1} given as the combination $4p^4$ $^1D_2$—5s′ $^2D^0$ and the intercombination $4p^4$ $^1D_2$—5s′ $^3D_2{}^0$ respectively. But the line 101532 defining the $4p^4$ $^1D_2$ level is distinctly classified as Br III $4p^3$ $^4S_{3/2}{}^0$—$4p^4$ $^4P_{5/2}$ combination (Bhupala Rao, 1956a). A search among the vacuum ultraviolet lines for the interval 5s′ $^1D^0$ —5s″ $^1P_1{}^0$ has led to the identification of the $4p^4$ $^1D_2$ level at 12098 and it is confirmed by its combinations with seventeen other odd levels. All these combinations are given in Table IV.

TABLE V

Odd levels		Even levels	4f $^5F_1$ 145941.1	$^5F_2$ 145937.3	$^5F_3$ 145932.9	$^5F_4$ 145929.9	$^5F_5$ 145931.6	$^3F_2$ 146087.5	$^3F_3$ 146081.6	$^3F_4$ 146095.1
$4p^5$	$^3P_0$	100242.2	45698.3 (2)							
	$^3P_1$	98807.3		47130.6 (0)						
	$^3P_2$	96439.4								
	$^1P_1$	113342.8						32745.0 (2)		
$4d$	$^5D_0$	104206.1	41734.7 (5)							
	$^5D_1$	104151.7	41789.6 (7)	41785.9 (8)						
	$^5D_2$	104086.1	41854.7 (4)	41851.2 (6)	41846 5 (9)					
	$^5D_3$	104044 6		41893.3 (4)	41890 5 (7)	41886 1 (10)				42051.0 (00)
	$^5D_4$	104097.9					41833.7 (10)			
	$^3D_1$	112395 9						33691.8 (8H)		
	$^3D_2$	111530 5						34557 4 (2)	34551 3(8H)	
	$^3D_3$	112460.5							33621.2 (5)	33634 6 (10H)
$5s'$	$^3D_1$	109428.2						36659.0 (5H)		
	$^3D_2$	109682.5						36404.7(1H)	36399.0(7H)	
	$^3D_3$	110378 2							35703.0(1h)	35716 4(5h)
	$^1D_2$	112939.5						33147.3 (2)	33141 6 (6h)	
$4d'$	$^3D_1$	126788.2						19299.6 (6)		
	$^3D_2$	127687.7			III? 18246.6 (0)			18399.9 (2)	18393.9 (6)	
	$^3D_3$	127940 6							18141.4 (3h)	18154.7 (10)

A search among the vacuum ultraviolet lines for the intervals of the ground term $4p^4\,{}^3P$, 701 and 3139, has led to the identification of the 4d′ $^3D^0$, $^1D^0$ terms (Table II). The presence of the 4d′ $^3D^0$—4f ^3F multiplet with good intensity (Table V) and the multiplet 4d′ $^3D^0$—5p″ ^3P (Table IV) point to their correct identification. But combinations of the 4d′ $^3D^0$ levels with 5p″ ^3D levels are only a few as can be seen in Table IV Starting with 4d′ $^3D^0$, $^1D^0$ terms it has been possible to arrive at the 4f′ (^3F, ^3D, ^1H, ^1G, ^1F, ^1D) and 4d′ ($^3F^0$, $^1G^0$, $^1F^0$) terms and the 4f′ $^3G_3$ level. The 4d′—4f′ combinations are all diffuse in varying degrees. The 4f′ ^3F, ^3D terms are inverted and their overall intervals are very small (−103.7 cm^{-1} −51.7 cm^{-1} respectively even though the interval between the ^2D levels of the parent configuration is 1195 cm^{-1}. The 4d′—4f′ combinations are given in Table VI and some of the multiplets are shown in Plate XII B.

The 4d″ levels could not be located since even with the most favourable estimate their combinations with the 5p′ and 5p″ levels are expected to occur beyond the photographic infra-red region; consequently it is not possible to identify the 4f″ levels also.

Several of the 5d′ and 6s′ levels given by Ramanadham and Rao had to be altered. The changes are discussed below.

1. The 5d′ $^3G_5{}^0$ level was fixed only by a single line 24529.2 cm^{-1}. This is classified otherwise as 5p′ $^3P_2$—5d′ $^3D_3{}^0$. Another line at 25010.2 cm^{-1} is taken as 5p′ $^3F_4$—5d′ $^3G_5{}^0$ consistent with the intensities of the combinations $^3F_2$—$^3G_3{}^0$ and $^3F_3$—$^3G_4{}^0$. The new level is 156756.6.

2. The levels 5d′ $^3F^0{}_{2,3}$ do not appear to be quite correctly identified. The combination 5p′ $^3F_3$—5d′ $^3F_3{}^0$ expected to be strong is absent and the combination 5p′ $^3F_2$—5d′ $^3F_2{}^0$ is also absent on the author's plates, probably not resolved from the stronger line 24983.4 cm^{-1} very close to it. The alternative levels suggested now are 157226.9 and 158327.4 for 5d′ $^3F_3{}^0$, $^3F_2{}^0$ respectively, which give strong $^3F_3$—$^3F_3{}^0$ and $^3F_2$—$^3F_2{}^0$ lines but the combinations with 5p′ ^3D levels are not of the expected intensity. Further, with the alternative choice the 5d′ $^3F^0$ term is inverted with a total interval of −1643.0 cm^{-1}. This is doubtful when the other 5d′ $^3G^0$, $^3D^0$ terms do not show this inversion or partial inversion. Therefore the levels designated by Ramanadham and Rao are retained and the two new levels 157226.9 and 158327.4 are given under the designations 5d′ $a^0{}_3$ and 5d′ $b^0{}_2$ respectively.

3. The magnitude of the 5d′ $^3D^0$ term identified by Ramanadham and Rao seemed to be too deep and inconsistent with the general progression of values 5d′ ^{3}(G^0, F^0, D^0, P^0, S^0) although the component levels are regarded as real. Hence the suggested 5d′ $^3D^0$ term is adopted as the 6s′ $^3D^0$ term, the identification of the latter being considered unsatisfactory. An entirely new set of levels is suggested as 5d′ $^3D^0$ term, the component levels being 157369.7, 157632.8 and 157808.3. The level 151458.3 given by Ramanadham and Rao as 6s′ $^3D_1{}^0$ is,

however, retained as a separate level b^0 since it gives three cobminations with $5p/^5P$ term though its combinations with all other levels are accounted for otherwise.

4. The 5d′ $^3P^0$ term also had to be altered, the 5d′ $^3P^0_1$ level having been regarded as 5d′ $^3D^0_2$ on account of the existence of another combination between this and 5p′ $^3F_3$. The level 5d′ $^3P^0_0$ was based on two lines 30581.9 and 25655.4 cm^{-1}. Of these, 30581.89 cm^{-1} is classified otherwise which makes the identification of the level uncertain. The two components of the 5d′ $^3P^0$ term newly identified are 159778.4 and 159910.8. The third component 5d′ $^3P^0_0$ level could not be located.

The designation and reality of the level 158234 are not certain; its combination with 5p′ $^3D_3$ (ν 27579.4) is accounted for otherwise (table 8). Hence the level is left out.

5. The identification of the 5d′ $^3S_1{}^0$ level was based on two lines one of which is not found on the author's plates. The other line 24448.5 cm^{-1} is now classified otherwise as $5s^{0''}$ $^3P^0_0$—5p″ $^3P_1$. The new level is 156512.2. It gives three combinations with 5p″ levels. Two of them are classified otherwise also but their intensity for the other combinations seems to be too large. Hence their double classification is considered justified.

6. Of the singlets, the level 5d′ $^1G_4{}^0$ was fixed by two lines, the important one among which (23295.9 cm^{-1}) is now classified otherwise as 5s″ $^3P^0_2$—5p″ $^3P_2$. The level 160887.7 identified as 5d′ $^1F^0_3$ has to be altered as 5d′ $^1D^0_2$ since it has given a combination with 5p′ $^1P_1$. The 5d′ $^1D^0_2$ has been assigned as 6s′ $^1D^0_2$, the magnitude of the level being consistent with the newly identified 6s′ $^3D^0$ levels. The two lines defining the 5d′ $^1P^0_1$ level are otherwise classified as combinations of the $4p^5$ $^1P^0_1$ level with 5p′ $^1D_2$, $^1P_1$. Hence the new identifications are made.

The 5d′ $^1G^0_4$ level is virtually based only one combination 5p′ $^1F_3$—5d′ $^1G^0_4$ (25273.7(5) cm^{-1}) the intercombination 5p′ $^3F_3$—5d′ $^1G_4{}^0$ (25655.4(00) cm^{-1}) being very weak. An alternative level is 158820.7 which gives the lines 27130.4 (3) and 27512.1 (4) cm^{-1}) with 5p′ $^1F_3$ and 5p′ $^3F_3$ respectively. But since the intensity of 27512.1 cm^{-1} is not only greater than that of the other line but much more than what can be reasonably expected for such an inter-combination, this level is not adopted as 5d′ $^1G_4{}^0$ and also not included in the table given in the preliminary note. All the 5p′—6s′, 5d′ combinations are given in Table III.

An attempt to identify the 6s″ and 5d″ terms with the help of ther intervals of the 5p″ levels has led to the identification of only the 6s″ $^3P^0_1$ level definitely and the 6s″ $^1P^0_1$, 5d″ $^1D^0_2$, $^1P^0_1$ levels with a certain amount of confidence. Other levels could not be suggested at all, the multiplets with these levels are too weak. But a number of levels are found with the anticipated order of magnitude.

Hence these are given as tentative levels in the preliminary note (1956) under the designations 6s″ a⁰ and 5d″ (a⁰, b⁰, c⁰ d⁰) suggesting their possible J values.

The level 138127.0 given by Ramanadham and Rao as 6s′ a is retained as a⁰ even though its reality is not yet confirmed.

IONISATION POTENTIAL

The absolute term values are calculated from the $^5S^0$ and $^3S^0$ terms of the '*ns*' series using the Rydberg formula. The values are found to be 5s $^5S^0{}_2$=81771.3 and 5s $^3S_1{}^0$=77552.7 with effective quantum numbers 2.317 and 2.379 respectively. When their separations from the ground level 93927.5 and 98476.4 are added they give 175698 and 176029 cm^{-1} respectively for the distance separating the ground levels of Br II and Br III. Their mean comes to 175869 cm^{-1}, the same value arrived at by Moore (1952).

From the *ns*′ $^3D_3{}^0$ levels converging to 4p^3 $^2D^0{}_{5/2}$ of Br II the absolute value of 5s′ $^3D^0{}_3$ is obtained to be 81908.6 giving the value 192286.8 for the limit 4p^3 $^2D^0{}_{5/2}$ of Br III reckoned from the ground level 4p^4 $^3P_2$ of Br II. The difference between the two limits is 16418 cm^{-1} which is in very good agreement with the interval 4p^3 $^4S^0{}_{3/2}$—4p^3 $^2D^0{}_{5/2}$ in Br III equal to 16300 cm^{-1} (Bhupala Rao, 1956a).

Though Moore has arrived at the value 175870 cm^{-1} (I.P. 21.80 V) for the limit, she has retained the value 174119 cm^{-1} (I.P. 21.6 V) given by Bloch, Bloch

TABLE VII

Configuration	Designation	J	Level	Interval
$4s^2\ 4p^4$	$4p^4\ ^1S$	0	27876	
$4s^2\ 4p^3\ (^4S)\ 6s$	$6s\ ^5S^0$	2	135794.3*	
$4s^2\ 4p^3\ (^4S)\ 6s$	$6s\ ^3S^0$	1	137608.0*	
	a^0	1	138127.0*	
$4s^2\ 4p^3\ (^4S)\ 5d$	$5d\ ^5D^0$	0	140223.5*	
				−0.8
		1	140222.7*	
				284.3
		2	140507.0*	
				−212.5
		3	140294.5*	
				−2.4
		4	140292.1*	
	b^0	2	151458.3*	
$4s^2\ 4p^3\ (^2P)\ 6s$	$6s''\ a^0$	2	166487.2	
$4s^2\ 4p^3\ (^2P)\ 6s$	$6s''\ ^1P^0$	1	167439.0	

TABLE VII (*contd.*)

Configuration	Designation	J	Level	Interval
$4s^2\ 4p^3\ (^2P)\ 5d$	$5d''\ a^0$	2 or 3	169127.6	
$4s^2\ 4p^3\ (^2P)\ 5d$	$5d''\ b^0$	2 or 3	169368.1	
$4s^2\ 4p^3\ (^2P)\ 5d$	$5d''\ c^0$	2	169676.2	
$4s^2\ 4p^3\ (^2P)\ 5d$	$5d''\ d^0$	2 or 3	169768.9	
$4s^2\ 4p^3\ (^2P)\ 5d$	$5d''\ ^1D^0$	2	170703.1	
$4s^2\ 4p^3\ (^2P)\ 5d$	$5d''\ ^1P^0$	1	170827.4	
Br III $(^4S^0_{1\frac{1}{2}})$	LIMIT		175870	

* Identified in previous investigations

TABLE VIII

Intensity	λ(air)	ν(vac)	Classification	Remarks
1	8725.3	11458	$4d'\ ^3F_3^0-5p'\ ^3D_2$	
0	8417.5	11877	$4d'\ ^3F_4^0-5p'\ ^3F_3$	
1	8231.0	12146	$4d'\ ^3F_3^0-5p'\ ^3D_3$	
1	7552.2	13238	$4d'\ ^3F_4^0-5p'\ ^3F_4$	Br I
0	6768.8	14770	$4d'\ ^3F_3^0-5p'\ ^3P_2$	
2	6168.49	16207.0	$5p''\ ^3D_3-5d'\ ^3P_2^0$	
00	5643.37	17715.0	$5s'\ ^1D_2^0-5p'\ ^3D_3$	
00	5611.42	17815.9	$5p''\ ^3D_1-5d'\ ^3P_2^0$	
4	5199.35	19227.8	$4d\ ^3D_3^0-5p'\ ^1F_3$	
2	5055.87	19773.5	$5p\ ^3P_0-6s\ ^3S_1^0$	
1	4941.24	20232.2	$5s'\ ^3D_3^0-5p'\ ^3F_2$	
2	4861.11	20565.7	$5p''\ ^3P_2-6s''\ a_2^0$	
3	4777.04	20927.6	$5s'\ ^3D_2^0-5p'\ ^3F_2$	
00vbb	4578.07	21837.2	$5p''\ ^3P_1-6s''\ ^1P_1^0$	
0	4465.18	22389.3	$5p\ ^3P_0-5d\ ^5D_1^0$	
1	4388.20	22782.0	$5p''\ ^3D_3-6s''\ a_2^0$	
0	4361.54	22921.3	$5p''\ ^1P_1-6s''\ ^1P_1^0$	
2H	4308.00	23206.1	$5p''\ ^3P_2-5d''\ a_2^0$ or 3	
1	4261.22	23460.9	$5s''\ ^3P_2^0-4f\ ^3F_2$	

TABLE VIII (*contd.*)

Intensity	λ(air)	ν(vac)	Classification	Remarks
2	4208.51	23754.7	$5p''\ ^1D_2-5d''\ a_2^0$ or 3	
			$5p''\ ^3P_2-5d''\ c_2^0$	
00	4192.40	23846.0	$5p''\ ^3P_2-5d''\ d^0_2$ or 3	
0	4129.33	24210.2	$4d\ ^5D_1{}^0-5p'\ ^1D_2$	
2	4118.56	24273.0	$4d'\ ^3F_4{}^0-5p''\ ^3D_3$	
1	4115.71	24290 3*	$5p''\ ^3P_0-6s''\ ^1P_1{}^0$	
1	4106.39	24345.5	$4d'\ ^3F_3{}^0-5p''\ ^3D_2$	
0	4105.50	24350.7	$4d'\ ^3F_2{}^0-5p''\ ^3D_1$	
1	4097.90	24395.9	$5p''\ ^1D_2-5d''\ d_2^0$ or 3	
0	4034.11	24781.6	$5p''\ ^3P_2-5d''\ ^1D_2{}^0$	
00	3963.18	25225.2	$5p''\ ^3P_1-5d''\ ^1P_1{}^0$	Br III line?
3	3946.86	25329.5	$5p''\ ^1D_2-5d''\ ^1D_2{}^0$	
0b	3944.55	25344.3	$5p''\ ^3D_1-6s''\ ^1P_1{}^0$	
00	3932.27	25423.4	$5p''\ ^3D_3-5d''\ a_2^0$ or 3	
0	3927.42	25454.8	$5p''\ ^1D_2-5d''\ ^1P_1{}^0$	
0	3895.52	25663.3	$5p''\ ^3D_3-5d''\ b_2^0$ or 3	
0	3850.94	25960.4	$4d'\ ^3F_2{}^0-5p''\ ^3D_1$	
0b	3849.28	25971.6	$5p''\ ^3D_3-5d''\ c_2^0$	
0	3835.82	26062.7	$5p''\ ^3D_3-5d''\ d_2^0$ or 3	
1	3817.85	26185.4	$5p''\ ^1P_1-5d''\ ^1D_2{}^0$	
2	3811.37	26229.9	$5s'\ ^3D_3{}^0-5p'\ ^1D_2$	
0b	3799.80	26309.7	$5p''\ ^1P_1-5d''\ ^1P_1{}^0$	
0	3778.43	26458.5	$5d\ ^5D_1{}^0-5p'\ ^3F_2$	
2h	3770.41	26514.8	$5p''\ ^3D_2-5d''\ b_2^0$ or 3	
1	3762.82	26568.3	$4d\ ^5D_2{}^0-5p'\ ^3D_3$	
1	3756.84	26610.6	$4d\ ^5D^0{}_3-5p'\ ^3D_3$	coincidence with a Br III line
1	3749.43	26663.2	$4d'\ ^3F_4{}^0-4f\ ^3F_4$	Br III line
00	3733.99	26773.4	$4d'\ ^3F_2{}^0-5p''\ ^1P_1$	
0	3727.29	26821.5	$5p''\ ^3D_2-5d''\ c_2^0$	Br III line?
3h	3725.46	26834.7	$5p''\ ^3S_1-5d''\ c_2^0$	?

TABLE VIII (*contd.*)

Intensity	λ(air)	ν(vac)	Classification	Remarks
00	3721.25	26865.1	$4d'\ {}^3F_3{}^0 - 5p''\ {}^1D_2$	
3	3714.45	26914.3*	$5p''\ {}^3D_2 - 5d''\ d^0{}_2$ or 3	
00	3712.93	26925.3	$5s'\ {}^3D_2{}^0 - 5p'\ {}^1D_2$	
2	3678.24	27179 2	$5s'\ {}^3D_1{}^0 - 5p'\ {}^1D_2$	
2	3624 87	27579 4	$4d'\ {}^3F_3{}^0 - 4f\ {}^3F_2$	
			$5p''\ {}^3D_1 - 5d''\ c_2{}^0$	
1	3623.88	27586.9	$4d'\ {}^3F_3{}^0 - 4f\ {}^3F_1$	
3	3622.06	27600.8	$4d\ {}^5D_2{}^0 - 5p'\ {}^1F_3$	
0	3615.92	27647.6	$4d\ {}^5D_4{}^0\ 5p'\ {}^3F_4$	
1	3608.98	27700.8	$4d\ {}^5D_3{}^0 - 5p'\ {}^3F_4$	
1	3527.98	28336.8	$4d'\ {}^3F_2{}^0 - 4f\ {}^3F_3$	Br III line
0h	3527.06	28344.2	$4d'\ {}^3F^0{}_2 - 4f\ {}^3F_2$	
00	3480.59	28722.6	$5p'\ {}^1D_2 - 6s''\ {}^3P_1{}^0$	
1	3432 33	29126.4	$4d\ {}^5D_1{}^0 - 5p'\ {}^3P_2$	
0	3419.82	29233.0	$4d\ {}^5D_3{}^0 - 5p'\ {}^3P_2$	
0	3400.93	29395.3	$4d\ {}^5D_0{}^0 - 5p'\ {}^3P_1$	
1	3397.88	29421.7	$4d\ {}^5D_1{}^0 - 5p'\ {}^3P_0$	Br III line
1	3387.18	29514.6	$4d\ {}^5D_2{}^0 - 5p'\ {}^3P_1$	
1	3310.28	30200.3	$5s\ {}^3S_1{}^0 - 5p'\ {}^3D_1$	
1	3174.66	31490.4	$5s\ {}^3S_1{}^0 - 5p'\ {}^3D_2$	
1h	3150.94	31727.4	$5p'\ {}^3P_1 - 6s''\ {}^3P_1{}^0$	
1	2958.07	33796.0	$5p\ {}^3P_1 - 6s'\ {}^3D_1{}^0$	
?	2945.55	33939.6	$5p\ {}^3P_1 - 6s'\ {}^3D_2{}^0$	coincidence with a Br III line?
0	2888.29	34612.4	$5p\ {}^3P_2 - 6s'\ {}^3D_3{}^0$	
00h	2834.41	35270.4	$5p\ {}^3P_1 - 6s'\ {}^1D_2{}^0$	
1H	2725.32	36682.1	$5s\ {}^5S_2{}^0 - 5p'\ {}^3F_2$	
00	2715.16	26819.4	$5p\ {}^5P_1 - 6s'\ {}^3D_2{}^0$	
2H	2578.66	38768.2	$4d\ {}^5D_2{}^0 - 5p''\ {}^3D_2$	
2	2393.32	41770.2	$4d\ {}^5D_1{}^0 - 5p''\ {}^3P_2$	
00	2372.05	42144.7	$5p\ {}^3P_2 - 5d'\ {}^3P_2{}^0$	

TABLE VIII (*contd.*)

Intensity	λ(air)	ν(vac)	Classification		Remarks
0	2344.92	42632.3	$5p\ ^5P_3–5d'$	$^3D_3{}^0$	Br III line
3	1410.2	70911	$4p^4\ ^1S_0–4p^5$	$^3P_1{}^0$	?
1	1226.3	81545	$4p^4\ ^1S_0–5s'$	$^3D_1{}^0$	
1	1170.2	85453	$4p^4\ ^1S_0–4p^4$	$^1P_1{}^0$	Br III line?
1	1029.0	97183	$4p^4\ ^1S_0–5s''$	$^1P_1{}^0$	
0	947.1	105591	$4p^4\ ^3P_0–5s'$	$^3D_1{}^0$	
0	889.9	112375	$4p^4\ ^3P_2–4d$	$^3D_1{}^0$	?
1	786.4	127160	$4p^4\ ^1D_2–5d$	$^3D_3{}^0$	
00	743.8	134454	$4p^4\ ^3P_1–6s$	$^3S_1{}^0$	
0	710.6	140726	$4p^4\ ^1D_2–6s'$	$^1D_2{}^0$	

* Also classified otherwise in previous investigations.

† double classification.

and Lacroute (1934) feeling that the new value is probably too high. Lacroute (1935, page 70) stated that the absolute values were obtained from the ns $^5S_2{}^0$ series and remarked that the calculation made from two terms could not be considered as very accurate. From the results of the calculations by Moore and in the present investigation it appears that Lacroute's estimate is in error On a perusal of the table of binding energies of electrons of singly-ionised atoms (Moore and Russell, 1952) the value derived for Br II on the basis of 174119 cm^{-1} for the limit seems to be too small and not consistent with the general progression of values in the first spark spectra of neighbouring elements. With 175870 cm^{-1}

TABLE IX

Spectrum	4p		4d		5s		5p		5d	
Se II	$4p^3\ ^4S_{3/2}{}^0$	21.5			$5s\ ^4P_{1/2}$	9.70	$5p\ ^4P_{1/2}{}^0$	7.50	$5d\ ^4F_{3/2}$	4 36
Bloch		21.6		—		9.94		7.37		4.32
Br II	$4p^4\ ^3P_2$		$4d\ ^5D_3{}^0$		$5s\ ^5S_2{}^0$		$5p\ ^5P_1$		$5d\ ^3D_3{}^0$	
Author		21.80		8.90		10.16		7.58		4.54
Kr II	$4p^5\ ^2P_{3/2}{}^0$	24.56	$4d\ ^4D_{7/2}$	9.66	$5s\ ^4P_{5/2}$	10.58	$5p\ ^4P^0{}_{5/2}$	7.96	$5d\ ^4P_{1/2}$	4.63

for the limit they appear to be of the right order of magnitude and are given in Table IX along with the old ones based on Bloch's value for the limit and those for Se II and Kr II.

A comparison of the effective quantum numbers $n^* = 4\ R/T$ corresponding to the deepest terms of the 5s electron in the first spark spectra of bromine and its neighbouring elements is made in Table X as in the case of As I. (Meggers, Shenstone and Moore, 1950).

TABLE X

Spectrum	Term	T (Absolute value)	$4R/T$	$n^* = (4R/T)^{1/2}$
Ga II	$5s\ ^3S_1$	62515	7.022	2.650
Ge II	$5s\ ^2S_{1/2}$	66116	6.639	2.577
As II	$5s\ ^3P_0{}^0$	84271	5.209	2.282
Se II	$5s\ ^4P_{3/2}$	78287.0	5.607	2.308
Br II	$5s\ ^5S_2{}^0$	81905.1	5.359	2.315
Kr II	$5s\ ^4P_{5/2}$	85352.0	5.143	2.268
Rb II	$5s\ ^3P_2{}^0$	88504.7	4.960	2.227
Sr II	$5s\ ^2S_{1/2}$	88964.0	4.934	2.221

By interpolation the value of n^* for 5s in Br II is obtained as 2.315. The corresponding term $T = 4R/(n^*)^2$ has a numerical value $(4\times 109737.1)/(2.315)^2 = 81905.1$ and gives the limit as 175832.6 cm^{-1} agreeing very well with the value derived from the "*ns*" series. This value 2.315 of n^* for 5s $^5S^0{}_2$ derived in this way is in good agreement also with the value 2.317 derived from the "*ns*" series. In view of the above considerations it appears that the value 175870 cm^{-1} for the limit may not be high and may be adopted as the limit corresponding to a second ionisation potential of 21.80 volts. This is therefore given as the limit.

Comparison with other spectra

A perusal of the final analysis shows that the term intervals are in general smaller than the separations between different terms and there is not much mixing up of levels of different terms. But the interval ratios within the terms are not in accord with the theoretical values derived from *L-S* coupling. The spectrum has very great resemblance to Kr III in several respects.

A comparison of the relative positions of $(n+1)s\ ^5S^0$, $nd\ ^5D^0$ and $np^5\ ^3P^0$ terms in the analogous spectra will be of interest here. The values are taken from Moore's "Atomic Energy Levels" Vols. I and II (1949 and 1952) and are collected in Table XI. The values of the limit and 4d $^5D^0{}_4$ for Br II are from the present analysis. A striking feature of the structure of these spectra is the increasing stability with atomic number of the np^5 and nd configurations. In both the isoelectronic sequences the $(n+1)$ $^5S^0$ term lies deepest in the first members, SI and SeI, followed by nd $^5D^0$ and np^5 $^3P^0$. In the case of the second members, Cl II and Br II, they are all of the same order and a crossing of the levels takes place.

TABLE XI

Spectrum	Limit	n	$(n+1)s$ $^5S_2{}^0$	nd $^5D_4{}^0$	np^5 $^3P_2{}^0$
S I	83559.3	3	52623.9	67878.0	72025.5
Cl II	192000	3	107878 5	110295.8	93366.6
A III	32996.58	3	174375.0	144907 0	113800.7
Se I	78658.2	4	48182.2	63370 1	—
Br II	175870	4	93927.5	104097.9	96439.4
Kr III	298020	4	145720.0	138650.3	115932

When we go to the third members, A III and Kr III, the order of the terms is np^5 $^3p^0$, nd $^5D^0$ and $(n+1)s$ $^5S^0$. The np^5 $^3p^0$ terms are all inverted. The intervals of the nd $^5D^0$ terms are all small and they are inverted except in A III and Kr III.

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